PART I

GENERAL

PHYSICS IN FISH PROCESSING TECHNOLOGY

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To design, develop and put into operation an equipment either to increase the productivity or to improve the existing technique to obtain a better quality of the product, the fishery engineer/scientist should have a comprehensive knowledge of fundamental principles involved in the process. Many a technique in fish processing technology, whether it applies to freezing, dehydration or canning, involves always a type of heat transfer, which is dependent to a certain extent on the external physical parameters like temperature. humidity, pressure, air flow etc and also on the thermodynamic properties of fish muscle in the temperature ranges encountered. Similarly informations on other physical values like dielectric constant and dielectric loss in the design of quick thawers and in quality assessment of frozen/iced fish, refractive index and viscosity in the measurement of the saturation and polymerisation of fish oils and shear strength in the judgement of textural qualities of cooked fish, are also equally important.

The impact of physics in fish processing technology can be seen in the development of sophisticated techniques/instrumentation needed for research like radio chromatography in biochemistry, Intelectron Fish Tester V based on the dielectric behaviour of fish tissue, physical techniques employing nuclear magnetic resonance and molecular absorption properties of water molecules (or hydrogen atom) as a measure of moisture in fishery products, electron microscopy for identification of bacteria and studying the ultra structure of fish muscle etc.

BIOPHYSICS IN FREEZING

Three important parameters, viz; apparent specific heat, thermal conductivity and ice/water fractions in frozen fish tissue, are required for the development of a suitable refrigeration system for freezing, thawing, cold storage or transport of frozen/chilled fish. Fish muscle contains protein, fat and organic and inorganic salts in solution. As the temperature of fish is progressively decreased below its initial freezing point, −1.1°C (corresponding to 0.28 M NaCl solution), inorganic salt solution throws out pure crystalline ice, itself getting more concentrated in the process. The freezing point of salt solution thus decreases and progressive freezing takes place following the pattern of freezing curve in Fig 1.

Thus the enthalpy (H) of the fish muscle of a given composition is a function

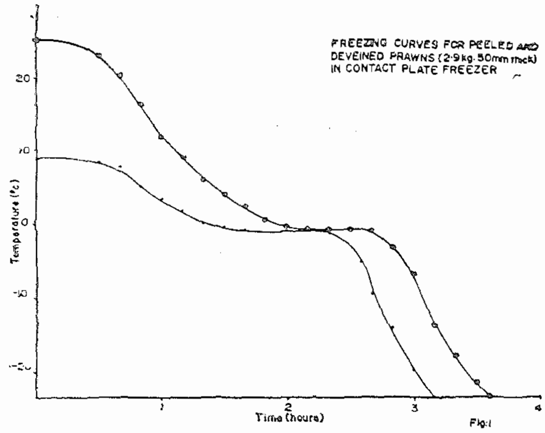


Fig.1

of temperature (θ) of fish. For thawing frozen fish most of the latent heat must be supplied in the temperature zone —5 to —1°C, so called 'thermal arrest' where $\left(\frac{dH}{d\theta}\right)$ becomes very large. This thermal arrest zone is of interest, as biophysical investigations have revealed that at critical freezing rate, when the muscle cools from 0 to —5°C in about 60 minutes, each cell contains just one ice crystal (Love 1962) and this is also dependent on the initial temperature of the the material (Long 1955, Perigreen, unpublished). This initial temperature effect is attributed partly to changes in thermal conductivity values of frozen and unfrozen fish tissues and partly to differential cooling rates. X-ray diffraction examination of the ice component of frozen fish muscle has revealed the common hexagonal form but with preferred crystallographic orientation of ice crystals (Aitken 1966). During freezing, proteins become increasingly dehydrated as more tightly bound water is freed and to avoid denaturation, low temperatures in freezing are to be avoided. Love (1963), in one of his classical investigations, has found that freezing of bound water at —78°C (and subsequent storage at —14°C) is irreversible. Riedel (1957) defines bound water to be water unfrozen at very low temperatures. It is actually chemically combined in the muscle at the rate of one molecule of water for every two molecules of amino acid ie; 0.385 kg water/kg of dry substance.

Since the thermal conductivity of frozen fish at —30°C is about 3½ times that of chilled fish at 1°C (Jason & Long 1955), for same temperature gradient it is easier to freeze than to thaw. However the electrical conductivity at low frequency of fully thawed fish is 250 times that of frozen fish at —28°C, a property utilized in the design of electrical resistance thawing (Sanders 1963). Enthalpy or apparent specific heat of fish in the freezing zone is considered to be the algebraic sum of specific heats of salt solution and ice, latent heats of solution of salt, melting of pure and eutectic ice and specific heats of protein gel and unfrozen water. Enthalpy measurements useful in the design of refrigeration equipment are worked out for cod, haddock, white fish etc by Riedel (1956) and Jason and Long *(loc cit.)* Fig 2. To work out ice requirements for chilling and storage of fresh fish, knowledge of specific heat of fish above 0°C is necessary. So also the thermal conductivity of fish above 0°C is important in arriving at optimum thickness of fish layer for rapid chilling by

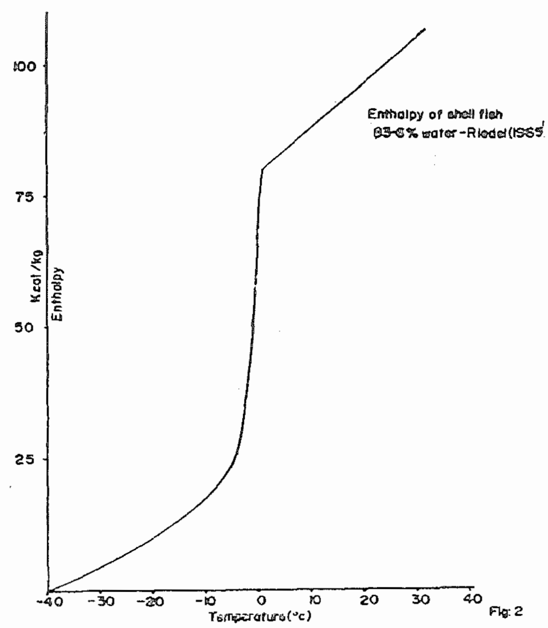


Fig 2

ice. The bottom of a 10 cm thick layer of prawns iced on the top will be at 10°C even after an interval of 3 hours due to poor conductivity of chilled fish (Rao 1968).

Kinetics of biological reaction rates and frequency factors for such reactions are studied to predict the physical and chemical changes the frozen fish undergoes during fluctuating or steady low temperature storage. Recent investigations try to link these changes to the unusual dielectric behaviour of frozen fish (Jason, unpublished). He has observed frozen cod muscle to exhibit characteristic resistance behaviour of intrinsic semiconductors like crystalline proteins. Energy of activation of protein denaturation is close to that of charge carriers and there is a possibility that protons are charge carriers and essential for the chemical process in the frozen state.

Knowledge of variation of density with temperature is required in the calculations of freezing or thawing times and bulk densities for stowage rates. The determination of density is purely theoretical (Long 1956) and as anticipated it falls as freezing proceeds, as large portion of moisture in fish is converted into ice.

Texture of processed fish, an important quality factor linked with the structural quality of the material, is often defined in terms of hardness, fluidity, elasticity, adhesiveness, chewiness etc. The manner in which these properties manifest themselves though difficult to analyse, can be expressed in terms of energy or power required to chew which can be measured in an equipment designed to determine its shear strength, elasticity and Poission's ratio to effect that change (Charm 1963).

Temperature and humidity

Temperature and humidity are other important physical parameters in fish preservation. It is observed that the rate of spoilage of fish is related to the temperature and at 2·5°C it would be twice as fast as at —1.1°C (Hess 1934). The storage life of a fish product at —18°C is reduced by six weeks if it is kept for 3 days at —9.5°C prior to storage at —18°C (Dyer *et al* 1957). Three types of portable instruments for temperature measurement of frozen and iced fish under field conditions are available (Jason and Lees 1959, Storey, 1965, Rao 1968) in the temperature range —30 to +30°C.

Humidity in the cold storages is required to be near saturation ie; the partial pressure of water vapour in air should be equal to the vapour pressure of ice on the surface of fish at the storage temperature (—30°C and below) to avoid dehydration (freezer burn) of frozen fish. Psychometric charts show that at these low temperatures, even a wet bulb depression of 0.5°C is enough to reduce the humidity from saturation by 5 to 6% and the drying potential could be easily imagined. The capacitance resistance hygrometer having anodised aluminium oxide as the dielectric material can be used with certain amount of accuracy at relative humidities above 90% and temperatures upto —15°C (Jason 1957). During initial stages of drying too, the drying rate of fish muscle is controlled by environmental conditions, of which humidity is an important parameter.

Drying and salting

Preservation of fish by salting and drying has been practised since long in developing countries. Yet approach to these practices had been mostly practical and empirical, scientific investigations into the basic mechanisms involved in the process being scanty (Jason 1958, Del Valle and Nickerson 1967). During initial stage of constant rate period, the drying rate of the fish muscle is controlled by external conditions and is equal to that from a saturated surface of same shape. The duration of this period is expressed by a relation containing the rate of evaporation per unit area, effective diffusion constant, thickness of fish sample and free water content. The subsequent falling rate has two distinct phases. The drying behaviour in the first phase is in accord with the solution of a diffusion equation based on Fick's law, the effective diffusion coefficient being independent of shrinkage of fish. The diffusion coefficient in the second phase is about 1/5th of that of the first phase. The transition from the first to second falling rate period appears to be associated with uncovering of the unimolecular layer of water which covers the protein molecule. The processes of evaporation and diffusion are characterized by a scheme of energy levels involving the heat of adsorption of unimolecular layer of water, the heat of liquefaction of water and activation energies corresponding to each of the two phases of falling rate periods. The effect of presence of fat is a reduction in the effective values of diffusion coefficients in the first and second phases of falling rate period.

Studying the dynamic aspects of salting of fish, Del Valle and Nickerson *(loc cit.)* observe that salt concentration in fish muscle and tissue water increases with brine concentration. The equilibrium distribution coefficient based on muscle volume and water content increases at first, passes through a maximum and then decreases with brine concentration. The distribution coefficient is roughly equal to unity and is independent of salt concentrtion in the brine. The migration of salt into the fish muscle, has been studied deeply by observing other factors like equivalent conductance and sodium and chloride ion transference number in muscle and water. The difussion coefficient and equivalent conductance of salt in fish muscle increase with temperature and time and are in agreement with predicted values. The activation energies for salt diffusion in fish muscle and in water of infinite dilution are found to be in the region of hydrogen bonding energies.

Other physical methods like measurements of optical density of fish muscle extract by colorimeter and refractive index and opacity of muscle fluid (Govindan 1964, Love 1962, Elerian 1965) for assessing the quality of ice stored prawns and fish, determination of the variation of electrical resistance with loss of moisture as a measure of bound water content in fish (Figure 3) (Akiba 1961), non-destructive type of testing freshness of edible fish by Fish tester V, based on the fact that the A. C. resistance of fish contains capacitative and resistive components which are conditioned by properties of cellular skins (Hennings 1964), (Figure 4), measuring cold storage changes in frozen fish muscle

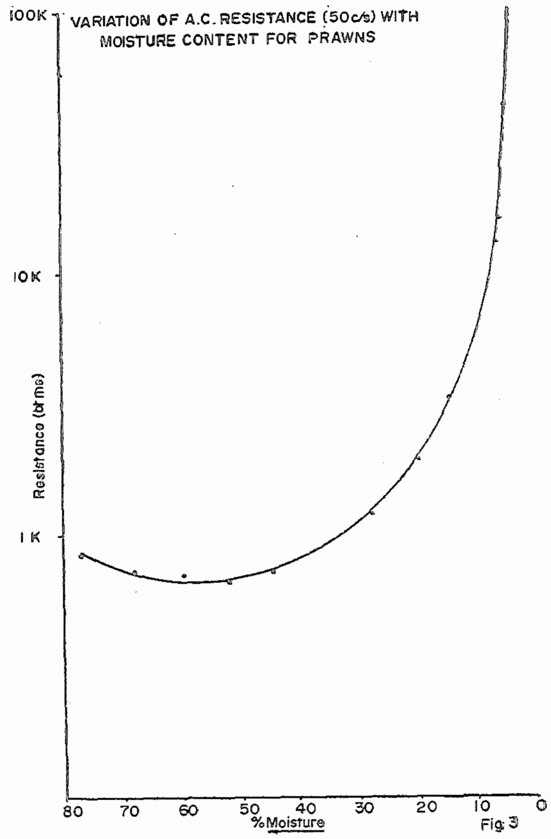
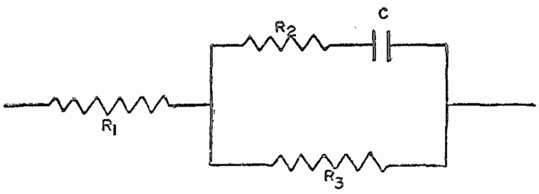


Fig. 3

COMPLEX RESISTANCE OF FISH CELL
(HENNINGS 1964)



R1 Resistance of interstitial liquid
R2 Resistance of cell content
R3 Resistance of cell wall
C Capacitance of cell wall

Fig: 4

TABLE I PHYSICIAL PROPERTIES OF FISH

1. Specific resistivity (50 c/s.) (Jason)
   -30°C 25×10^6 ohm/cm
   0°C 800 ,,
2. Dielectric constant (40 Mc/s) (Jason)
   —30°C 3
   0°C 65
3. Thermal conductivity (Jason & Long)
   + 1°C 1.30 Cal/cm² / Sec/°C/cm $\times 10^3$
   -10°C 3.96 ,,
   -20°C 4.40 ,,
4. Specific heat (Riedel)
   -40°C 0.44 Kcal/kg/°C
   +20°C 0.89 Kcal/kg/°C
5. Enthalpy for shell fish (83.6% water) (Riedel)
   Between -40 & + 20°C 94.38 Kcal/kg
6. Thermal diffusivity (Jason)
   -30°C 10.4 m^2 h^{-1}
   0°C 1.5 ,,
7. Initial freezing point depression — 1.1°C.
8. % water frozen (Mahadevan)
   -7°C 86%
   -12°C 91%
9. Bound water (Riedel) freezing at
   -70°C 0.385 g water/g total solid
10. Density -21.1°C 60.31 lbs/ft³
    -1°C 65.79 lbs/ft³

Bulk density (whole fresh fish) Waterman 62.5 lbs/ft³

,, (whole gutted frozen cod) 55 lbs/ft³ (compact packing)

by the cell fragility apparatus (Love 1962), determination of quantity of smoke constituents deposited during smoke curing by smoke density integrator (Storey 1966) etc illustrate the significant role of physics both in fish processing research and quality assessment of fishery products. Some of the physical properties of fish are summarised in Table 1.

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CORRIGENDUM

In our Volume VI no 2, page 116 last sentence, please read "treatment no 3" instead of "treatment no 4"